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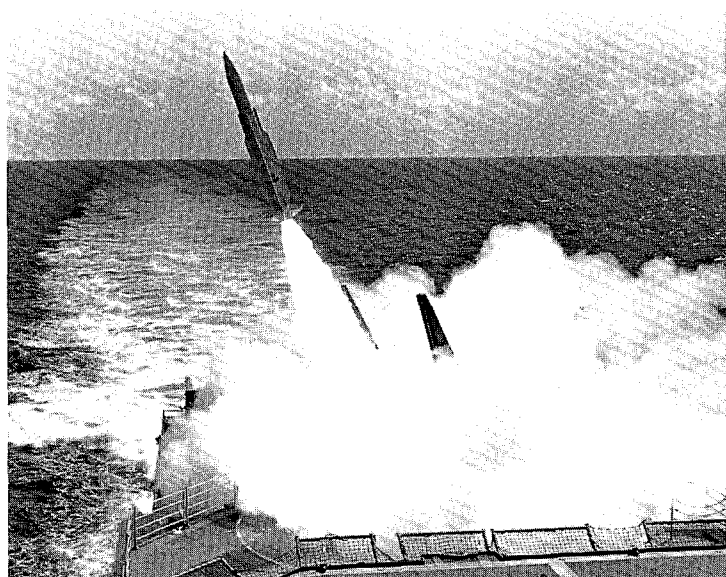


NSWC-MP-87-258

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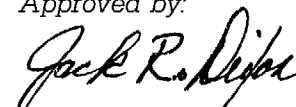
Foreword

The principal function of the Materials Division is to conduct research and development in support of the Center's mission. Towards this end, we carefully select our technical programs based upon anticipated future needs of the Center. Because of this, our endeavors typically result in the development of

highly mission-oriented capabilities and facilities. These capabilities are characterized by unusual breadth, ranging from research and exploratory development to engineering services. All of these program components are strongly coupled so as to maximize their effectiveness.

This brochure describes our capabilities and facilities in the areas of battery and corrosion technologies.

Approved by:



JACK R DIXON, Head
Materials Division

Contents

	Page		Page
Naval Surface Warfare Center	1	Reinforced Lead Grids	12
Electrochemistry Branch	2	Exploratory Development — Advanced Systems	13
Functions, Range, Emphasis, and Materials	3	Applications Engineering and Safety	14
Batteries—Complex Electrochemical Systems ...	4	Corrosion Technology	15
Electrochemical Batteries in the Navy	5	Specialized Facilities and Equipment	16
Present Technology	6	Thermal Analysis Facility	17
Future Batteries	7	Primary Power Sources for Naval Applications	18
Functions of the Electrochemistry Branch	8	Secondary Power Sources for Naval Applications	19
Research and Development Areas	9	Organization	20
Research	10	Personnel	21
Exploratory Development — Improving Conventional Systems	11		

Naval Surface Warfare Center

The Naval Surface Warfare Center (NSWC)* is the Navy's largest research, development, test, and evaluation (RDT&E) center. With primary locations at White Oak, Maryland, and Dahlgren, Virginia, the Center's mission is "to be the principal Navy RDT&E center for surface ship weapons systems, ordnance, mines, and strategic systems support."

NSWC was formed in 1974 with the consolidation of two Naval Material Command laboratories—the Naval Ordnance Laboratory, White Oak, and the Naval Weapons Laboratory, Dahlgren. Among the technology areas represented in the Center's effort are:

- Surface Ship Electronic Warfare
- Strategic Systems (including Reentry Technology)
- Mine Systems
- Nuclear Weapons Effects
- Biological and Chemical Warfare Systems
- Directed Energy Weapons Systems
- Explosive and Propellants Research Technology
- Mine, Torpedo, and Projectile Fuzes
- Combat Systems Engineering and Integration
- Materials Research and Technology
- Surface Weapons Systems
- Mine, Torpedo, Projectile, and Missile Warheads



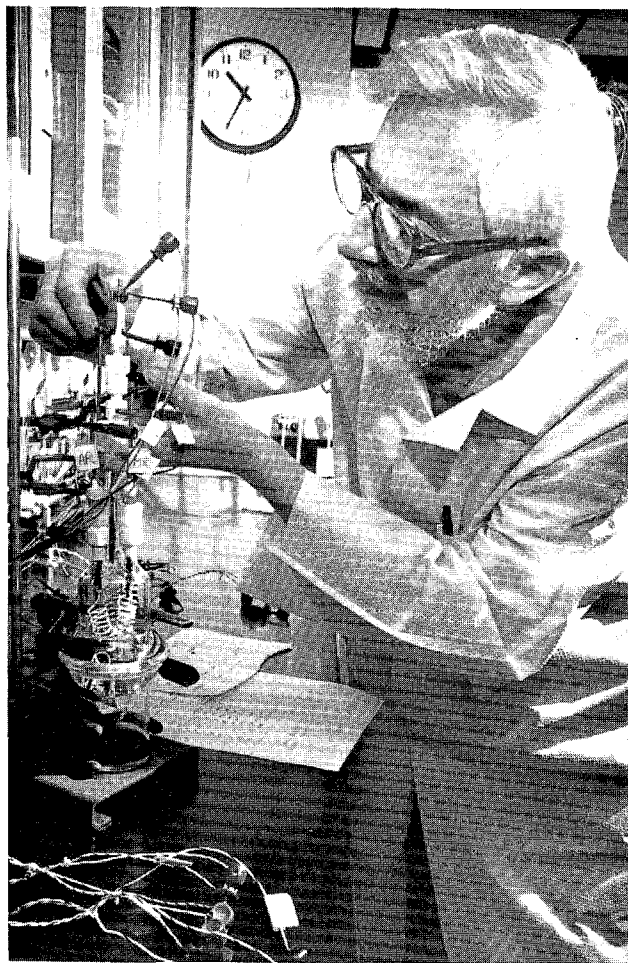
Naval Surface Warfare Center, White Oak, Silver Spring, Maryland

*NSWC was formerly the Naval Surface Weapons Center.

Electrochemistry Branch

The Electrochemistry Branch of the Naval Surface Warfare Center includes research and development in the areas of advanced electrochemical power sources and corrosion. The Branch is organizationally located in the Materials Division of NSWC's Research and Technology Department at White Oak, Maryland.

This publication is an overview of the Electrochemistry Branch and includes descriptions of the resources, capabilities, and technology available.

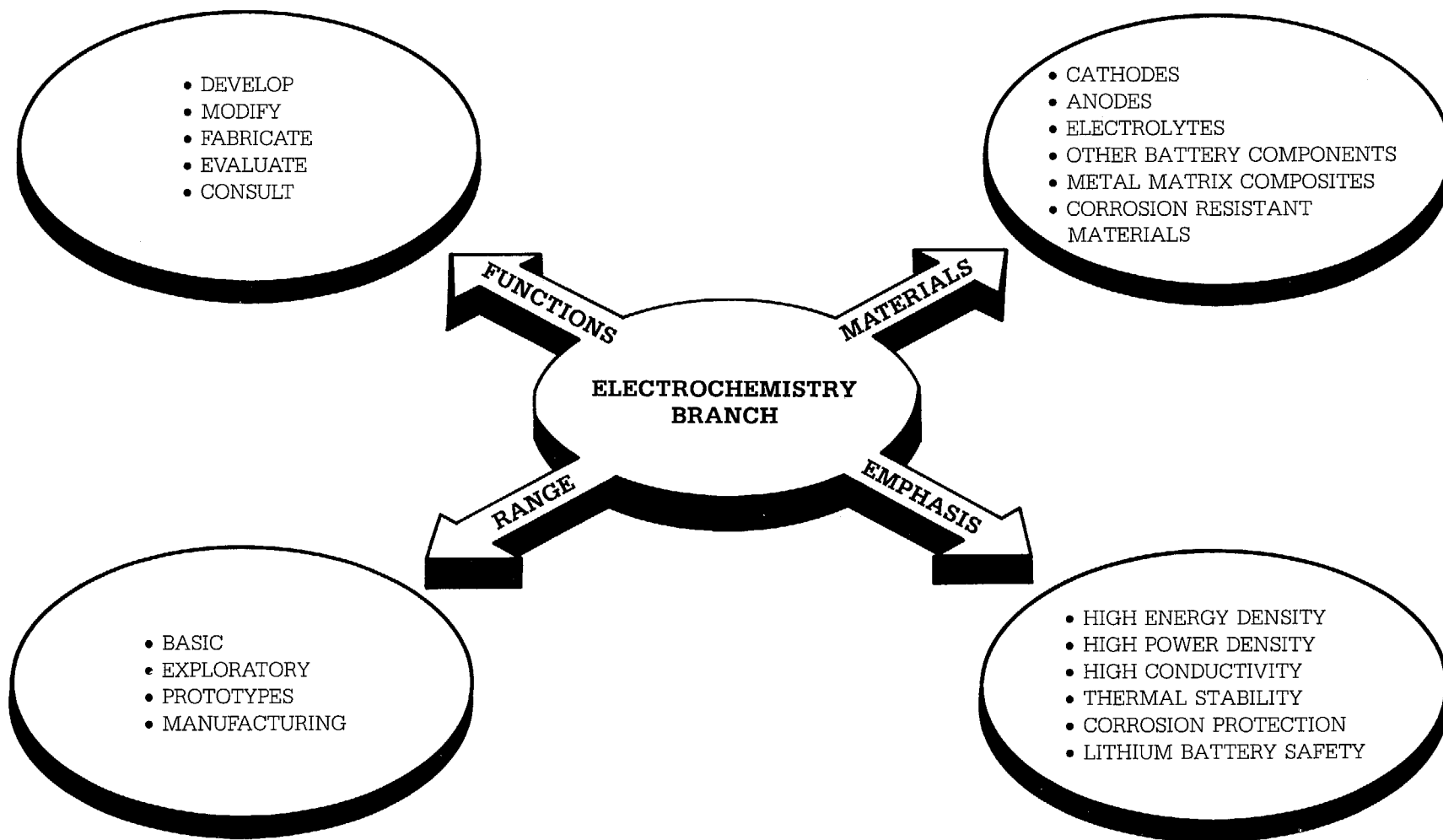


Performing Research on a New Battery Electrolyte

Mission

- Establish and maintain a broad technology base in areas of electrochemistry, battery science, and corrosion which directly supports the mission of the Center.
- Initiate, plan, and conduct research and exploratory development programs that advance the state of the art and provide new and improved electrochemical power systems for use in advanced weapon systems.
- Provide battery support for in-service and fleet applications.
- Provide consulting and engineering services to personnel from NSWC, from the Systems Commands, from other government laboratories, and from appropriate contractors.

Functions, Range, Emphasis, and Materials



Batteries—Complex Electrochemical Systems

A battery is a device for generating an electric current by chemical reaction. The basic building block of a battery is the electrochemical cell, whose main components are the anode, the cathode, and the electrolyte.

The chemical reactions that take place in a battery are:

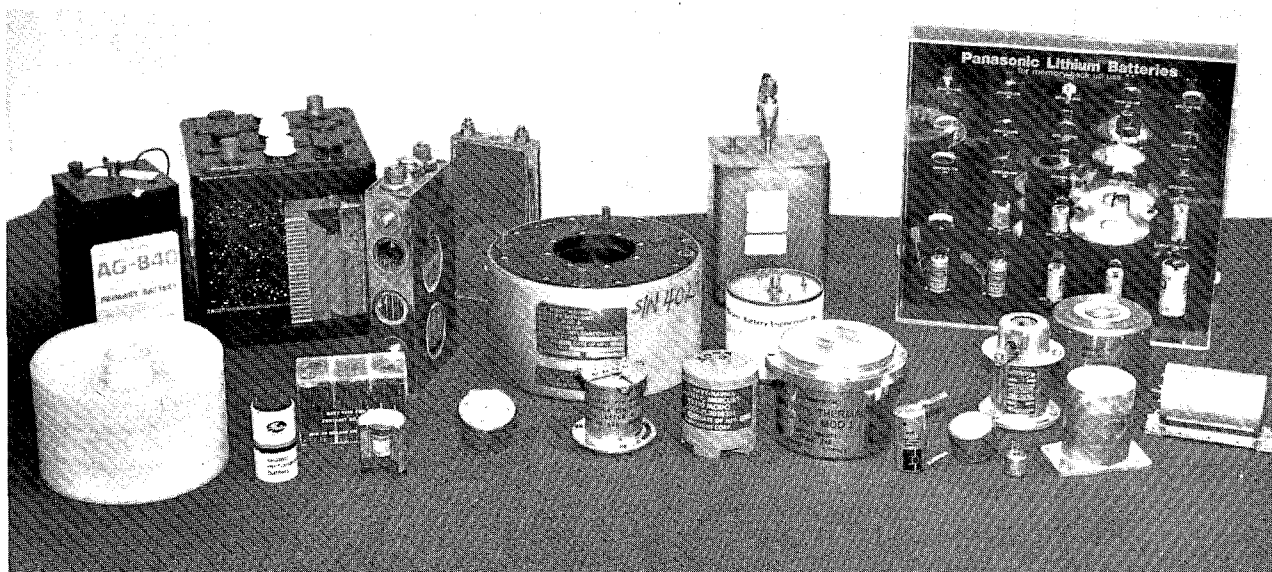
- The anode gives up electrons (oxidation)
- The cathode accepts electrons (reduction)

In a chemical reaction, electrons are exchanged directly. In an electrochemical cell, the electrons—by the simple means of separating the anode and the cathode by an ionic conductor (the electrolyte)—are forced through an outer-circuit and thereby do useful work.

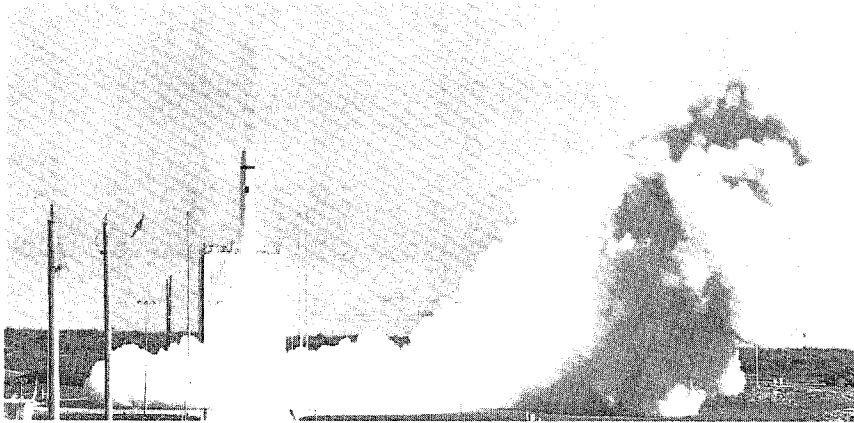
Important terms used in battery technology are:

- Voltage
- Current
- Power = voltage \times current
- Energy = voltage \times current \times time
- Power density = power / electrode area
- Energy density = energy / battery weight

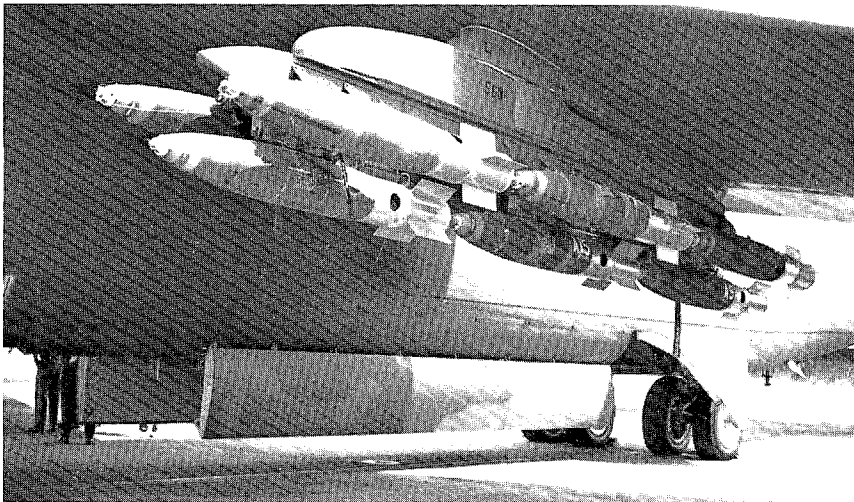
Typical Primary Active Batteries



Electrochemical Batteries in the Navy



TRIDENT (upper left) and STANDARD Missiles (right) Use High Energy Density Silver-Zinc Batteries



QUICKSTRIKE Mines Developed at NSWC Use Several Advanced Batteries



Present Technology

Electrochemical batteries today are needed to power devices that perform the following general functions in weapons systems:

- Detection
- Fuzing, Safety, and Arming
- Guidance and Control
- Propulsion (weapons and vehicular).

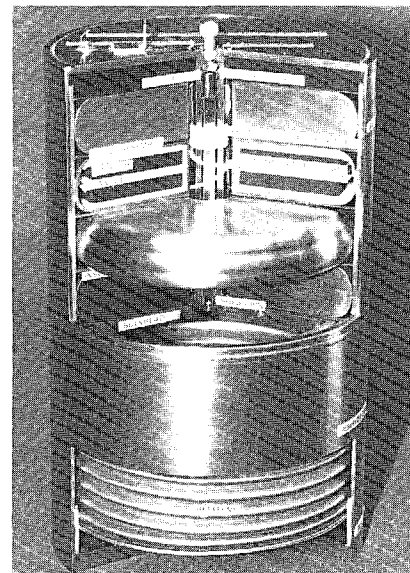
General requirements for these functions include high energy density, long (uncontrolled) shelf life, short start-up times, reliability, safety, the capability to operate over wide ranges of temperature, and extreme ruggedness.

Battery technology today is very complex, because optimal power sources for different

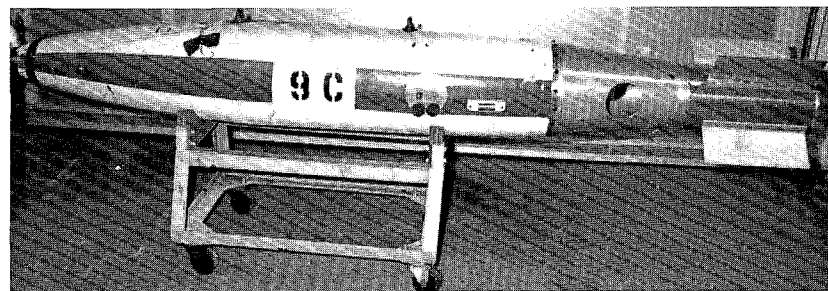
functions have to be based on different electrochemical couples. Thus, the needs of low-rate applications, such as detection (mines, sonobuoys, etc.), are satisfied by the Mg/MnO_2 , the HgO/Zn , or the Mg/AgCl (sea water) electrochemical systems.

Fuzing, safety, and arming devices (high-rate, short-time applications) utilize molten salt (thermal) batteries or the Pb/PbO_2 (fluoroboric acid) system.

Currently, the missile guidance and control function can best be performed by high rate Li/FeS_2 (thermal) or AgO/Zn (alkaline) batteries. The latter is widely used in propulsion systems (torpedoes, targets, submarines, etc.) in both the primary and the secondary versions.



Reserve Lithium Thionyl Chloride Battery Prototype for Advanced Mine



Versatile Exercise Mine

Future Batteries

Future weapons will need electric power sources with higher energy and power densities and with further improvements in voltage regulation, ruggedness, and storage capability. Electrochemical batteries will continue to be the principal portable power sources for Navy weapons until well into the next century.

The power source needs of the new "brilliant" weapons will have to be satisfied by new battery technology. In addition to the stricter requirements (energy density, etc.), many of the materials currently used in batteries (such as silver, zirconium, nickel, etc.) will have to be replaced in future batteries because critical shortages are predicted if current use patterns persist.

New technology will be based primarily on the use of lithium as the anode material. In elec-

trochemical systems, this metal, which is the lightest metal known, exhibits exceedingly high energy.

Batteries based on lithium anodes coupled with SO_2 , SOCl_2 , SO_2Cl_2 , or other high energy compounds can deliver energy densities four to five times higher than previous technology. This new technology, however, also necessitates a completely new approach to batteries. Most materials used are air and moisture sensitive, therefore not only research and development (R&D) but manufacturing also has to be carried out in specially constructed inert atmosphere glove boxes or dry rooms (1% relative humidity). Some materials might be toxic and therefore special procedures have to be observed in use and disposal as well as in fabrication. Finally the use of highly energetic materials pack-

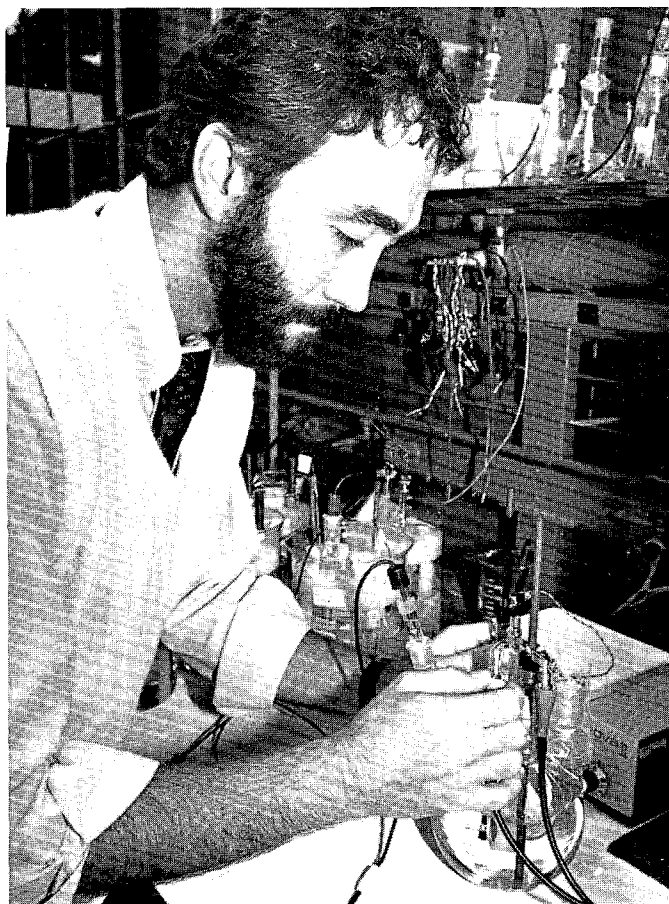
aged into very small space increases the danger of explosion should malfunction of these batteries occur. Hazardous incidents, including fires, explosions, and the release of toxic materials have been documented for some kinds of lithium batteries. The successful exploitation of promising new lithium battery technology will require careful attention to assure the safety of Navy personnel.

It is therefore imperative that extensive R&D be performed aimed at the determination of the properties of the materials used and at the understanding of the chemical and electrochemical processes involved and that the results of the R&D be translated into rigorous, well understood and documented manufacturing, use and disposal procedures.

Functions of the Electrochemistry Branch

The major functions of the Electrochemistry Branch are:

- Research:
Materials and electrochemical technology
- Exploratory Development:
New systems or improved components for systems already in use
- Applications Engineering and Safety:
Advanced and engineering development, testing, and evaluation for naval weapons
- Corrosion
Research and engineering studies to implement the Surface Warfare Combat Systems Corrosion Control Program (SWCSCCP)
- Consultation:
All aspects of battery research and technology, applications, and safety



Performing Electrochemical Corrosion Testing

Research

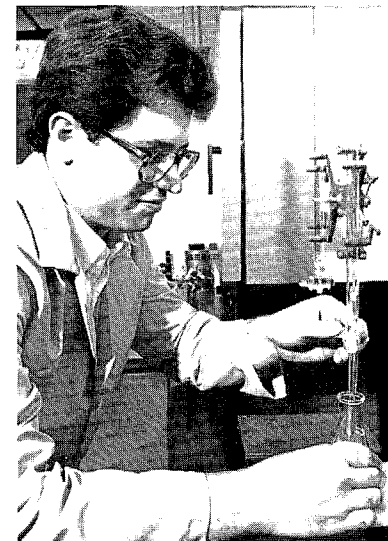
Research in the Electrochemistry Branch centers around battery systems that are of current or future interest as power sources in Navy weapons. These include:

- Low-rate, long-life primary batteries (used mainly in mines), such as the Leclanche dry cell, the alkaline MnO_2 and the alkaline Hg systems and more recently, the Li-organic or -inorganic cathode systems.
- New high energy Li batteries that are safer (less toxic and shock-sensitive) than first-generation Li technology.
- High-rate primary batteries (used in fuzing, arming, and safety, as well as missile guidance and control and torpedo propulsion), such as the thermal (molten salt) and the AgO/Zn systems.
- High-rate secondary batteries (used in submarines and deep submergence rescue vehicles),

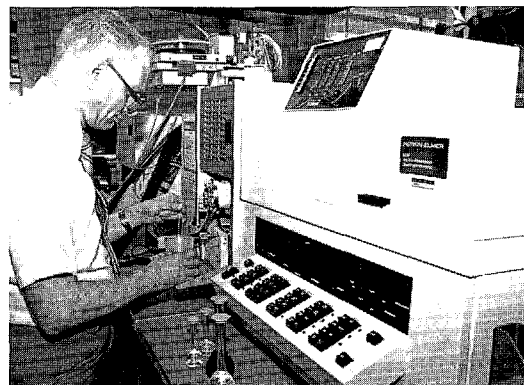
such as the rechargeable lithium systems being developed which should give improved energy density and cycle life over the currently used AgO/Zn system.

The Electrochemistry Branch is actively engaged in research on the following:

- Decomposition kinetics of cathode materials
- Thin cell technology for thermal batteries
- Rechargeable lithium batteries
- Catalysis of lithium batteries
- Novel lithium electrochemical couples
- Lab cell and battery hardware design and construction
- Characterization and control of corrosion

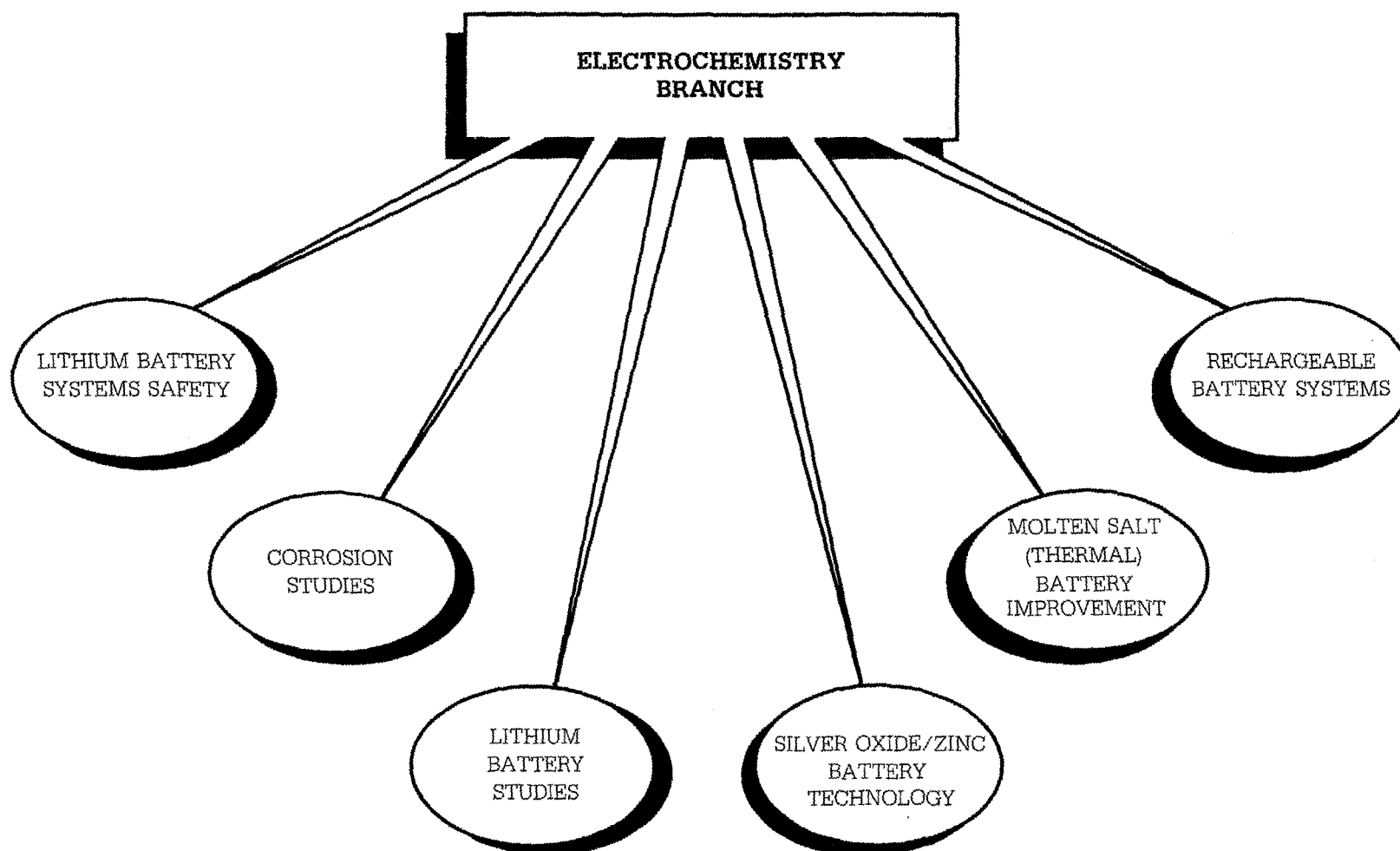


Conducting Titration of Battery Electrolyte



Performing Atomic Absorption Analysis of Battery Materials

Research and Development Areas



Exploratory Development — Improving Conventional Systems

The objective of exploratory development in the Electrochemistry Branch is to show the feasibility and practicability of new electrochemical systems or improvements to existing systems. Past achievements include the development of analytical methods to determine the quality of silver oxide material in silver oxide-zinc battery systems, the development of lithium-thionyl chloride reserve batteries, and reinforced lead-acid grids.

Current projects intended to improve existing systems are:

- Development of improved electrode materials for lead-acid batteries. The objective of this

project is to investigate the corrosion resistance of lead composites and lead alloys that might improve the cycle life and energy density of submarine batteries.

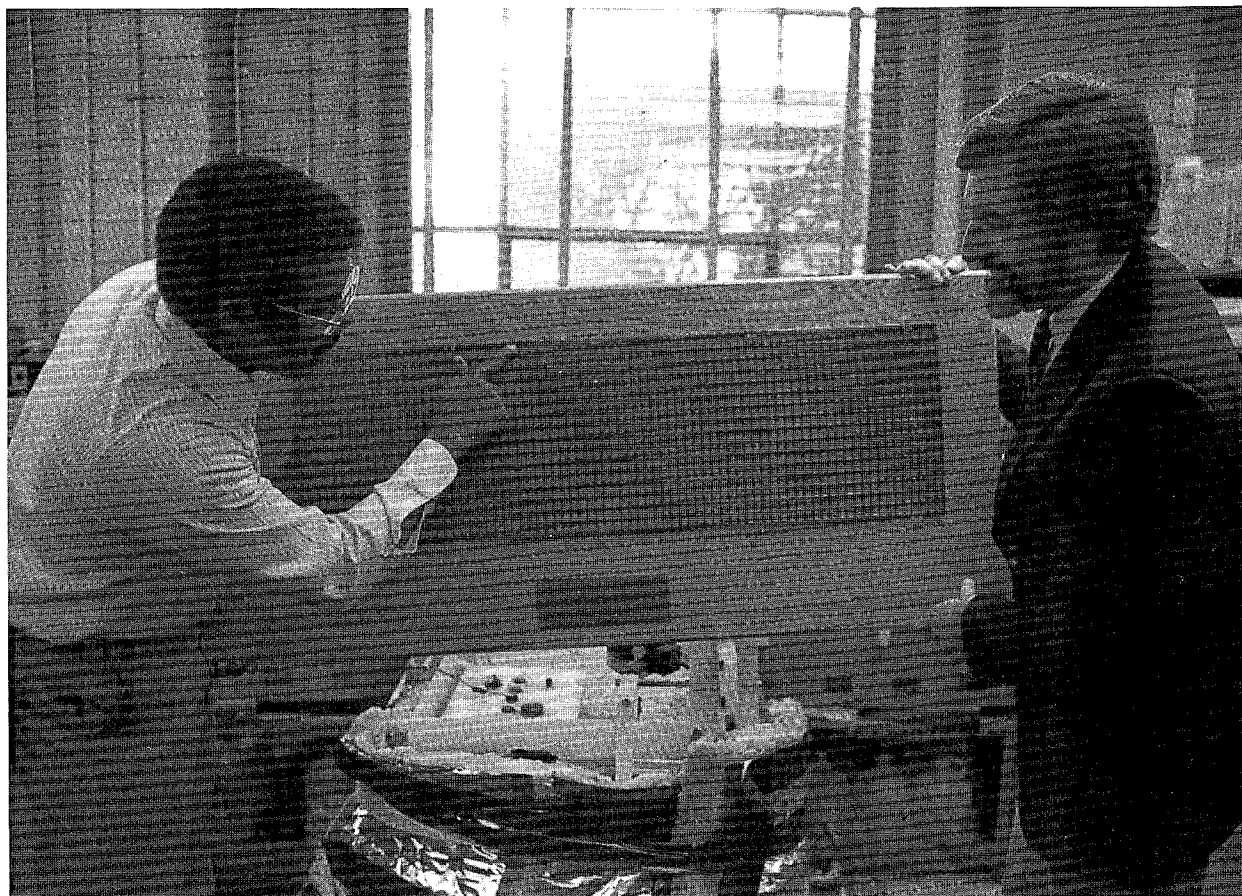
- Failure analysis of fleet batteries. The branch has a fully equipped Analytical Chemistry Lab with battery tear-down facilities. Information gained from analysis is used to improve batteries currently in production.



Determining Impurities in Battery Electrodes by Gas Chromatography

Reinforced Lead Grids

The Electrochemistry Branch, in collaboration with the Metallic Materials Branch, has developed a new composite battery grid to replace the lead grid previously employed in lead-acid batteries. This was in response to a critical fleet need to increase service life of submarine batteries. The new grid material consists of a reinforced-lead matrix composite, and it is unique in its low rate of corrosion compared to conventional lead alloy grids. This development is considered a major breakthrough in battery material technology.



Reinforced-Lead Matrix Composite Battery Grid

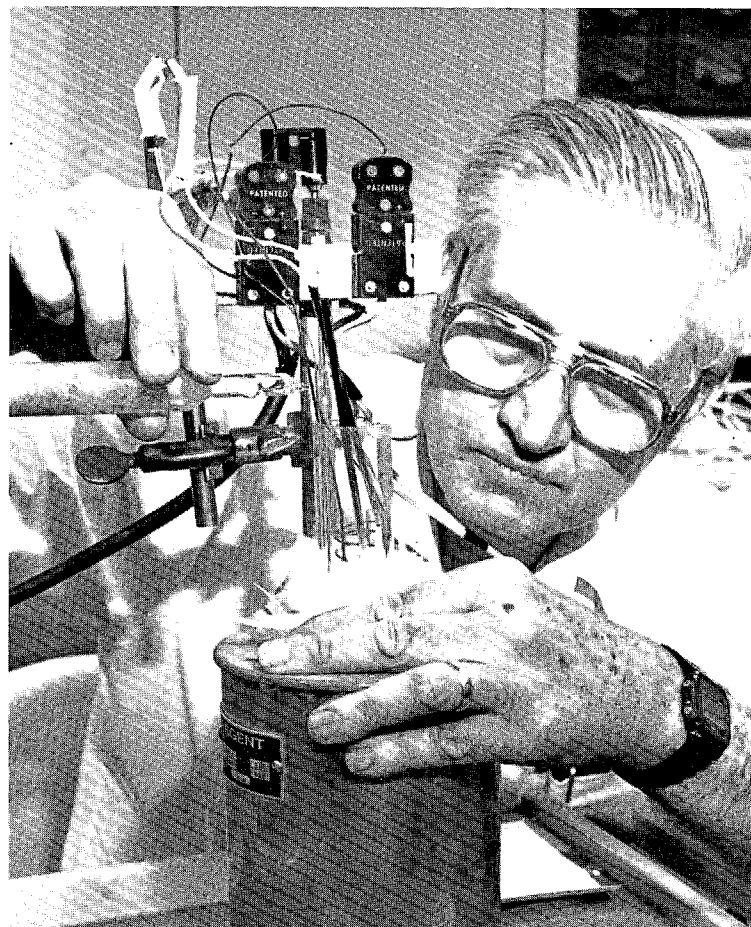
Exploratory Development—Advanced Systems

New technology explored in the Electrochemistry Branch centers around improvement and development of advanced battery systems. These systems have high power and energy densities. Technology is being developed in several projects:

- Development of a very high energy density, low rate battery for mines. The electrochemical system consists of a lithium anode and a sulfur dioxide cathode in conjunction with an organic-solvent-based electrolyte.
- Development of an improved, longer-life molten salt (thermal) battery. Thermal batteries do not deteriorate even after

many years of storage, but are limited by short discharge life. Synthesis of iron disulfide cathode material, thin cell technology, and computer simulation models are being developed to extend the discharge life and power capabilities.

- Improvements of silver-zinc reserve batteries. Silver-zinc reserve batteries have high power and energy densities but sometimes degrade quickly on the shelf. Research into the basic chemistry of the materials and into the processing of these materials at the manufacturer is being performed to increase the shelf life.



Performing Exploratory Studies on a New Molten Salt Battery Cathode Material

Applications Engineering and Safety

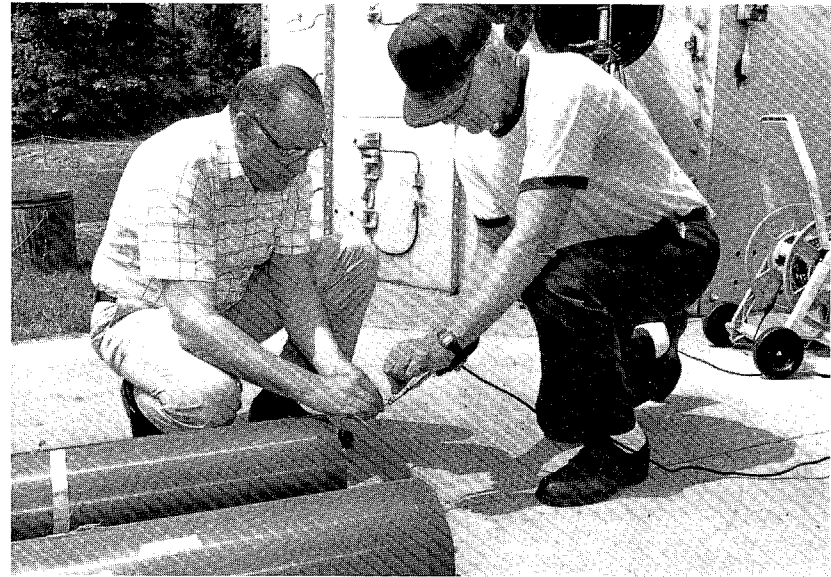
The Electrochemistry Branch has traditionally developed the batteries for every ordnance product of the Naval Surface Warfare Center, White Oak. Batteries developed in this Branch are now used in missiles (POLARIS, SHRIKE, SUBROC, TERRIER); bombs (HOTPOINT, SNAKEYE); torpedoes (ASROC, MK 37, MK 43); mines (Destructors MK 36 and MK 40, Mines MK 50-57); and other applications (Swimmer Launched Charge, Reentry Vehicles Mk 12 and Mk 17, LAD, SECT, etc.).

Present projects include the development of batteries for:

- QUICKSTRIKE (mercury active, mercury reserve, thermal, and lithium)
- CAPTOR (magnesium-manganese dioxide, SOCl_2 , thermal, and lithium)
- Advanced Sea Mine (lithium-liquid cathode)

NSWC serves as the Navy's lead laboratory for Lithium Battery Safety and is responsible for the review of every lithium battery proposed for Navy use.

Engineering development is carried out jointly with private industry. The Branch's expert staff creates a climate for success by strong leadership in selecting contractors; soliciting proposals; monitoring the development, production engineering, and quality control process; and writing specifications and design disclosures.



Preparing for a Safety Test of a Lithium Battery

Corrosion Technology

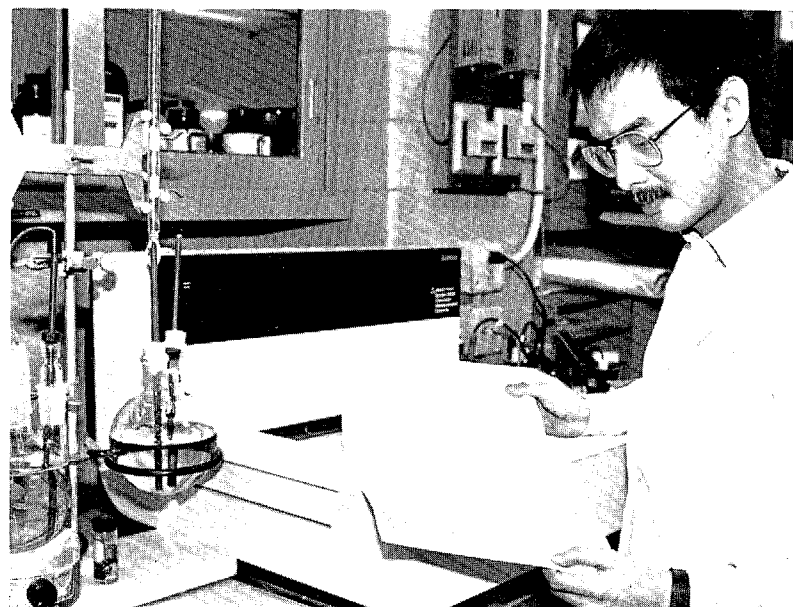
Atmospheric corrosion of metals and alloys, particularly in marine environments, is the most prevalent form of deterioration. The Corrosion Technology Group has extensive laboratory facilities for short-term accelerated tests of corrosion rate and a field testing facility for studying long-term rates.

NSWC is lead laboratory for the Surface Warfare Combat Systems Corrosion Control Program (SWCSCCP) and performs the following tasks:

- Develops supplemental guidelines for prevention and control of corrosion;
- Identifies current corrosion problem areas;
- Consolidates corrosion problem reports and maintains a computerized data base;
- Provides guidance to maintenance activities for corrosion control implementation;
- Reviews Engineering Change Proposals to determine corrosion control/preservation implications;
- Conducts corrosion research and engineering studies and investigations;
- Participates in intra- or inter-service information exchange programs;
- Conducts shipboard surveys on selected equipments to identify and resolve corrosion problems.



Real Time Testing of Corrosion Rates in Marine Environment

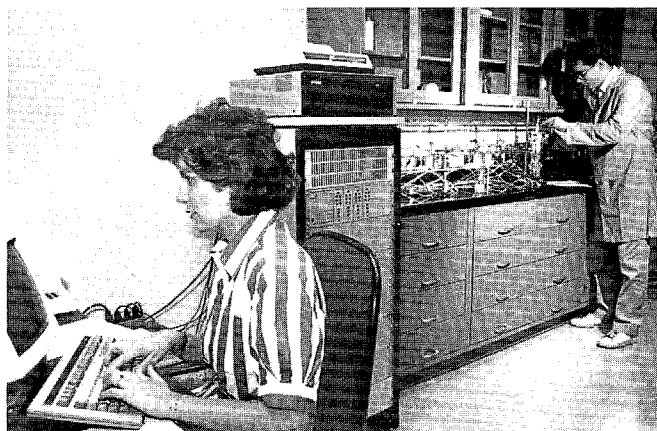


Studying Corrosion Behavior of Metal Matrix Composites

Specialized Facilities and Equipment

The Electrochemistry Branch has the following specialized facilities:

- Corrosion testing laboratory
- Battery testing laboratory
- Analytical laboratory
- Electrochemical research laboratory
- High energy battery storage and testing facility
- Dry room
- Thermal Analysis Facility

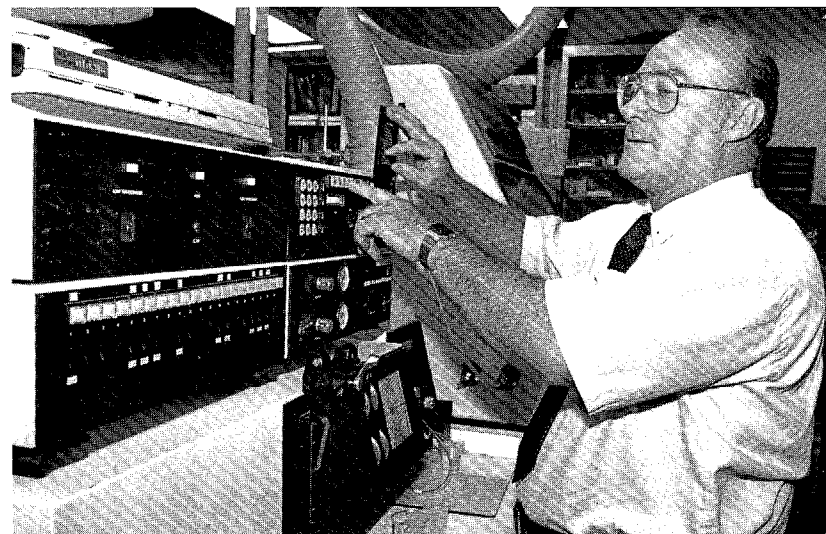


Experimental Lithium Cells Discharged on Computerized Battery Cycler

The Electrochemistry Branch has specialized equipment to perform:

- Polarography
- Cyclic voltammetry
- Potentiography
- Coulometry
- Spectroscopy (AA and FTIR)
- Calorimetry
- Gas chromatography

- Differential scanning calorimetry
- Thermomechanical analysis
- Differential thermal analysis
- Thermogravimetric analysis
- Metallography
- Microscopy
- Inert atmosphere preparations (glove boxes)



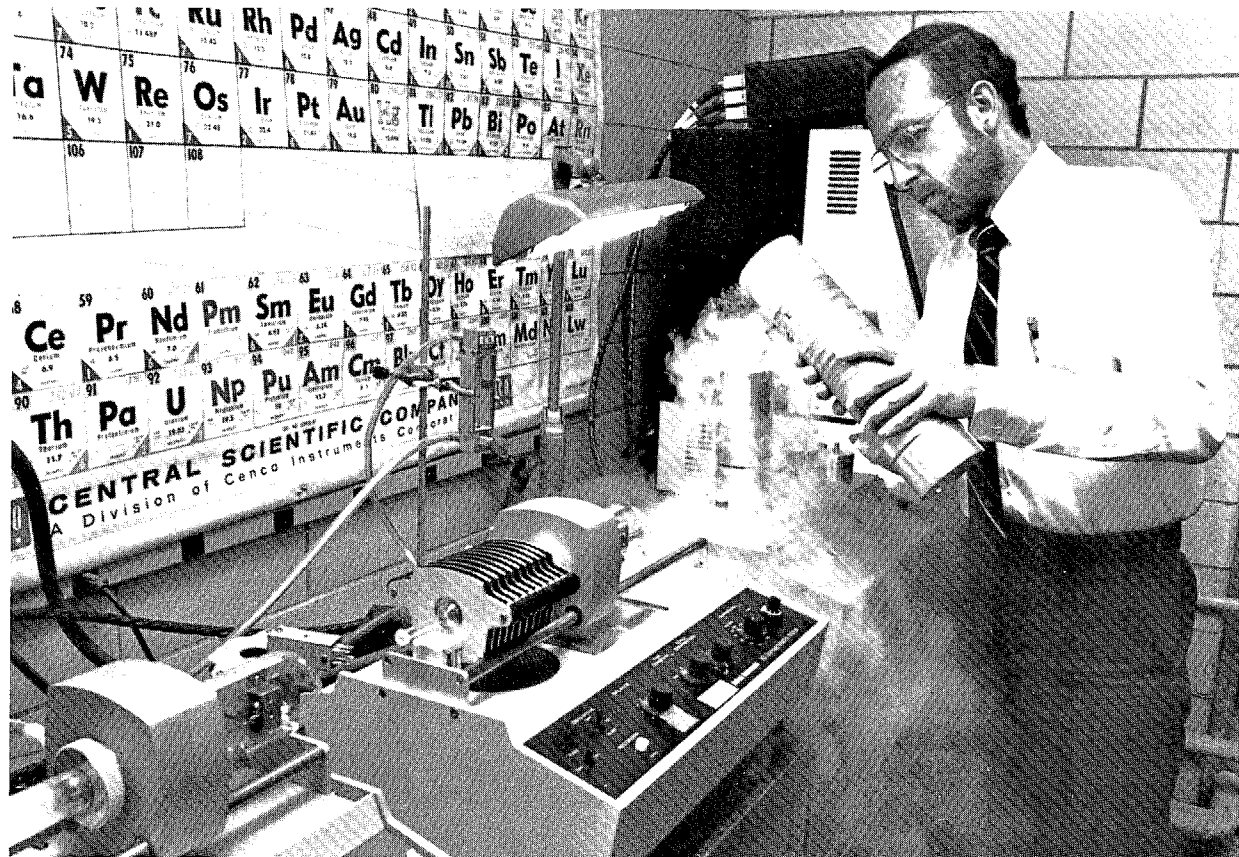
DC Argon Plasma Spectroscopy Used for Failure Analysis of Batteries

Thermal Analysis Facility

The Electrochemistry Branch houses the Naval Surface Warfare Center's Thermal Analysis Facility. This facility, which is jointly staffed by members of the Metallic Materials, Non-metallic Materials and Electrochemistry Branches, contains state-of-the-art equipment for carrying out research programs on a wide variety of materials, such as battery materials, shape memory alloys, amorphous alloys, ceramics, polymers, metal matrix composites, and explosives. Techniques which are routinely used include:

- Differential Scanning Calorimetry
- Thermogravimetric Analysis
- Thermomechanical Analysis
- Dynamic Mechanical Analysis
- Differential Thermal Analysis

In addition to innovative research conducted by the staff, the Thermal Analysis Facility provides services to a large number of groups throughout the Navy.



Performing Thermal Analysis Studies on a Cathode Material

Primary Power Sources for Naval Applications

CELL TYPE	⊖ ANODE MATERIAL	⊕ CATHODE MATERIAL	ELECTROLYTE	OPEN CIRCUIT VOLTS	TYPICAL WORKING VOLTS	TYPICAL SPECIFIC ENERGY	
						WATT HOURS/ POUND	WATT HOURS/ CUBIC INCH
COMMON DRY (LE CLANCHE)	Zinc, Zn	Manganese Dioxide, MnO ₂	Ammonium and Zinc Chlorides, NH ₄ Cl, ZnCl ₂	1.60	0.9–1.4	20–30	1.0–2.0
	Typical Uses: Mines, Communication Gear, Portable Lights. Characteristics: has low cost; sloping voltage, poor storability.						
ALKALINE DRY	Zinc, Zn	Manganese Dioxide, MnO ₂	Potassium Hydroxide, KOH	1.50	0.9–1.4	30–40	1.5–2.5
	Typical Uses: Same as above. Characteristics: has better high current and storage characteristics than Le Clanche.						
MERCURY (RUBIN)	Zinc, Zn	Mercuric Oxide, H ₂ O	Potassium Hydroxide, KOH	1.35	1.3	35–45	4.0–6.0
	Typical Uses: Reference Voltages, Mines, Communication Gear, Survival Equipment. Characteristics: standard OCV, flat discharge voltage, moderate storability, moderate cost.						
MAGNESIUM DRY	Magnesium, Mg	Manganese Dioxide, MnO ₂	Magnesium Bromide, MgBr ₂	2.4	1.5–1.6	40–45	3.0–3.5
	Typical Uses: Communication and Survival Gear, Mines. Characteristics: good storability, exhibits a voltage delay, generates hydrogen gas.						
LITHIUM-SULFUR DIOXIDE*	Lithium, Li	Sulfur Dioxide, SO ₂	Lithium Bromide, LiBr Lithium Hexafluoroarsenate LiAsF ₆	2.9	2.7–2.8	150	8.0–10
	Typical Uses: Underwater Devices, Mines, Communication and Survival Gear. Characteristics: excellent storability, low temperature performance, voltage regulation, and specific energy, may be hazardous.						
LITHIUM-THIONYL CHLORIDE*	Lithium, Li	Thionyl Chloride, SOCl ₂	Lithium Chloroaluminate, LiAlCl ₄	3.6	3.4–3.5	300	15–20
	Typical Uses: Under development for underwater devices. Characteristics: potentially excellent storability, excellent voltage regulation and specific energy, exhibits a voltage delay, may be hazardous.						
SILVER-ZINC (AUTOMATICALLY ACTIVATED)	Zinc, Zn	Silver Oxide, AgO	Potassium Hydroxide, KOH	1.86	1.35–1.45	30–40	2.0–3.0
	Typical Uses: Torpedoes, Mobile Mines, and Missiles. Characteristics: excellent high rate performance, voltage regulation, and storability; high cost; poor low temperature performance, silver is a scarce material.						
ZINC-AIR	Zinc, Zn	Air (Oxygen, O ₂)	Potassium Hydroxide, KOH	1.36	1.1–1.2	65	3.7
	Typical Uses: Potentially useful for special low rate underwater devices; Surface Buoys.						
SEAWATER (AUTOMATICALLY ACTIVATED)	Magnesium, Mg	Silver Chloride, AgCl	Seawater	~ 1.9	1.0–1.5	30–40**	
	Typical Uses: Torpedoes, Sonobuoys, and Survival Gear. Characteristics: has high cost; silver is a scarce material; performance is decreased by parasitic current, low temperature, and low salinity.						
FUZE ENERGIZER (AUTOMATICALLY ACTIVATED)	Lead, Pb	Lead Dioxide, PbO ₂	Fluoboric Acid, HBF ₄	2.06	1.4–1.8	15***	
	Typical Uses: Projectile and rocket fuzes. Characteristics: extremely rugged; high spin rate operation; good low temperature, high rate discharge, and storage characteristics.						
CALCIUM THERMAL (THERMALLY ACTIVATED)	Calcium, Ca	Calcium Chromate, CaCrO ₄	Molten Chlorides of Lithium and Potassium	~ 2.65	2.0–2.5	10–15†	
	Typical Uses: Missiles, Rockets, Mines, and Bombs. Characteristics: excellent for high power, short duration applications; extremely rugged; has the best demonstrated uncontrolled storage life of any of the known batteries.						
LITHIUM THERMAL (THERMALLY ACTIVATED)	Lithium, Li	Iron Sulfide, FeS ₂	Molten Chlorides of Lithium and Potassium	1.95	1.7–1.8	25††	
	Typical Uses: Under development as a replacement for calcium thermal. Characteristics: has demonstrated much higher specific power and energy than calcium thermal.						

*Other cathode materials such as carbon monofluoride (CF), cupric sulfide (CuS), manganese dioxide (MnO₂), and vanadium pentoxide (V₂O₅), have been used with lithium anodes in commercial cells but are not currently under development for any Navy applications.

**Includes the weight of enough seawater for a single fill.

***The gravimetric specific energy of a cell is about 15 Watt-hour per pound. However the weight of the structure needed for ruggedization coupled with the short run time results in a reduction of the specific energy of a battery to about 0.3 Watt-hour per pound.

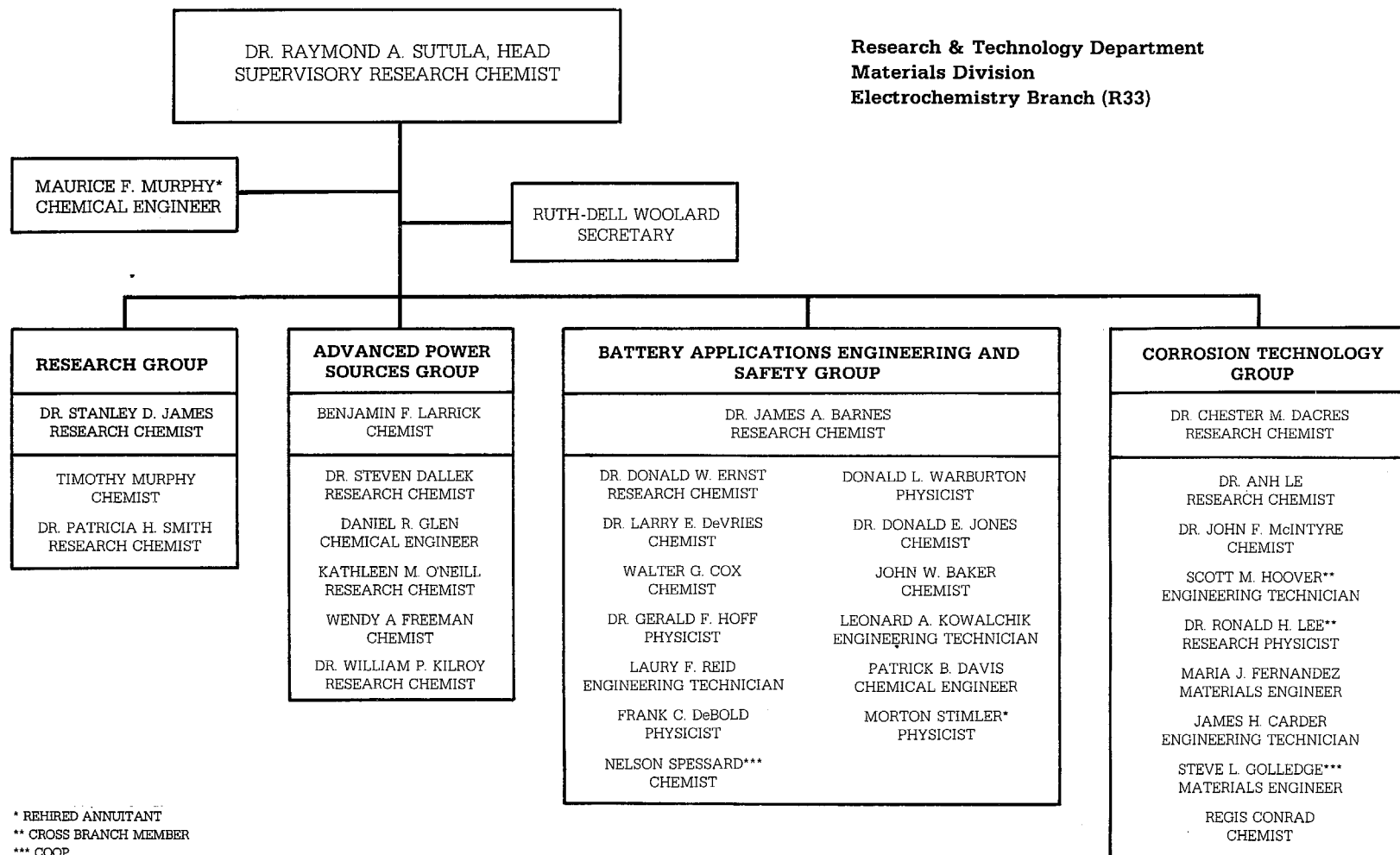
†The gravimetric specific energy of a cell is 10–15 Watt-hours per pound. The weight of ruggedizing and insulating materials typically reduces the gravimetric specific energy of a battery to about 3.0 Watt-hours per pound.

††The weight of ruggedizing and insulating materials reduces the gravimetric specific energy to 15–20 Watt-hours per pound.

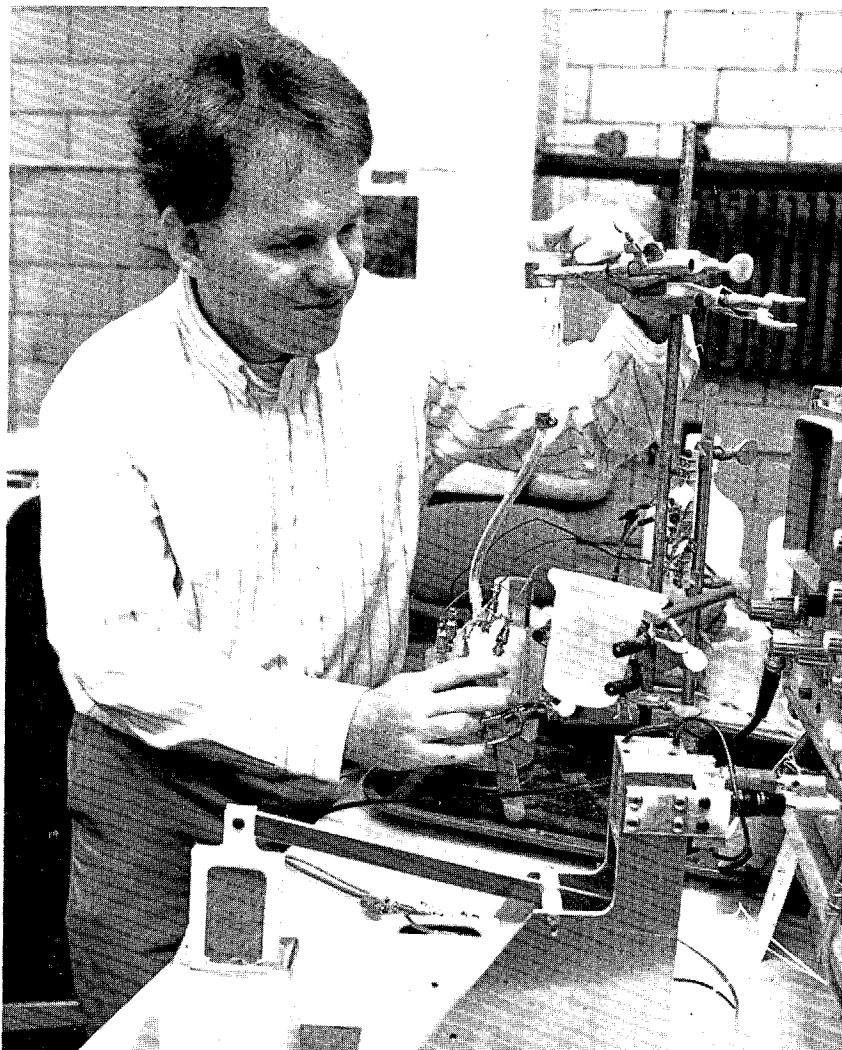
Secondary Power Sources for Naval Applications

CELL TYPE	⊖ ANODE MATERIAL	⊕ CATHODE MATERIAL	ELECTROLYTE	OPEN CIRCUIT VOLTS	TYPICAL WORKING VOLTS	TYPICAL SPECIFIC ENERGY		CYCLE LIFE
						WATT- HOURS/ POUND	WATT- HOURS/ CUBIC INCH	
LEAD ACID	Lead, Pb	Lead Dioxide, PbO ₂	Sulfuric Acid, H ₂ SO ₄	2.1	1.9–2.0	5–10	1.0–1.4	1000–2000
NICKEL-IRON (EDISON)	Iron, Fe	Nickel Oxide, NiO ₂	Potassium and Lithium Hydroxides	1.3	1.20–1.25	9.0–10	1.0	1000–3000
NICKEL-CADMIUM (SINTERED PLATE)	Cadmium, Cd	Nickel Oxide, NiO ₂	Potassium Hydroxide	1.3	1.20–1.25	10–15	1.0	250–1000
NICKEL-CADMIUM (POCKET PLATE)	Cadmium, Cd	Nickel Oxide, NiO ₂	Potassium and Lithium Hydroxides	1.3	1.20–1.25	10	1.0	1000–2000
SILVER-ZINC	Zinc, Zn	Silver Oxide, AgO	Potassium Hydroxide	1.86	1.2–1.5	25–40	2.0–3.0	10–40
NICKEL-ZINC	Zinc, Zn	Nickel Oxide, NiO ₂	Potassium Hydroxide	1.7	1.6	25–35	3.0	200

Organization



Personnel

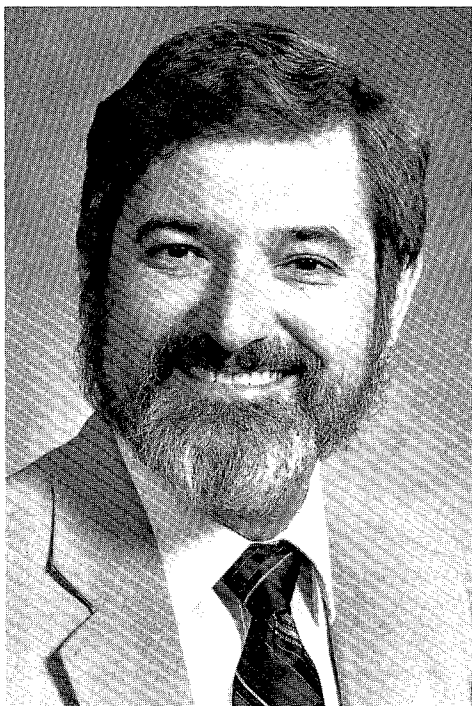


The staff of the Electrochemistry Branch includes twenty-five professionals (13 PhD and 14 BS Degrees) and three technicians skilled in electrochemical technology. While the scientific background of the professional staff varies (it includes degrees in chemistry, physics, and chemical engineering), they have all

specialized in the electrochemical aspects of their respective disciplines. The senior members of the staff are well known and highly respected in the scientific community and are often called upon for consultation by the Department of Defense and other agencies.

Personnel in the Electrochemistry Branch Perform Research, Exploratory Development, and Applications Engineering

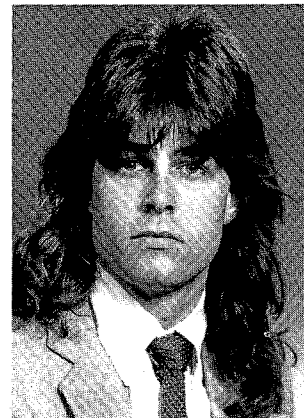
Personnel



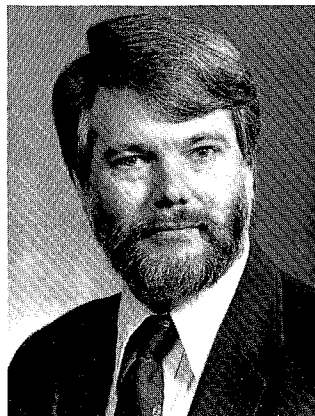
Dr. Raymond A. Sutula



Ruth-Dell Woolard



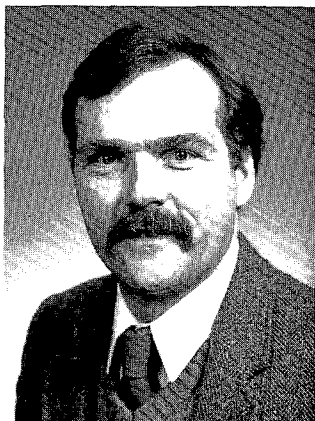
John W. Baker



Dr. James A. Barnes



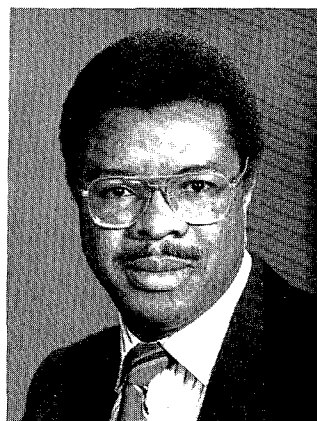
James H. Carder



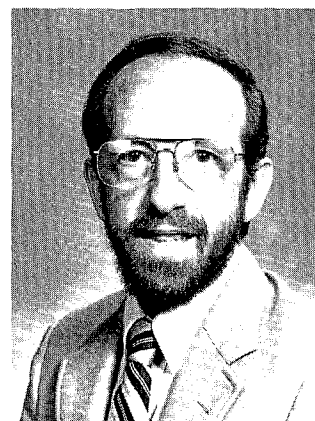
Regis Conrad



Walter G. Cox



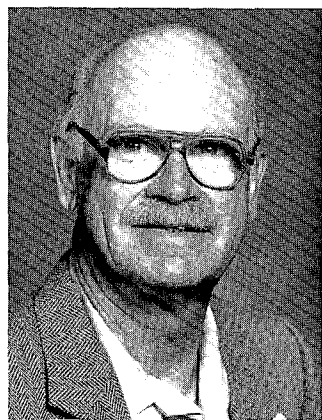
Dr. Chester M. Dacres



Dr. Steven Dallek



Patrick B. Davis



Frank C. DeBold



Dr. Larry E. DeVries



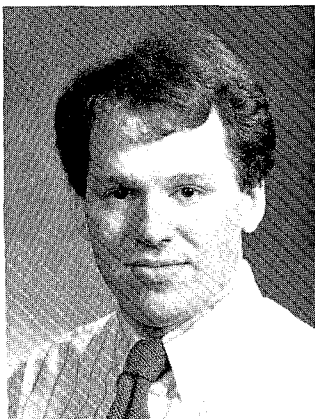
Dr. Donald W. Ernst



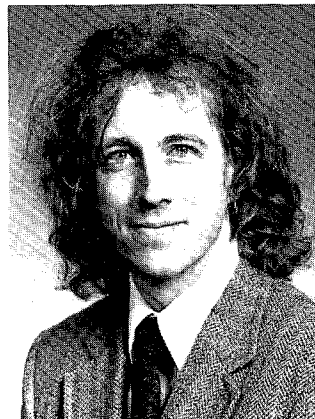
Maria J. Fernandez



Wendy A. Freeman



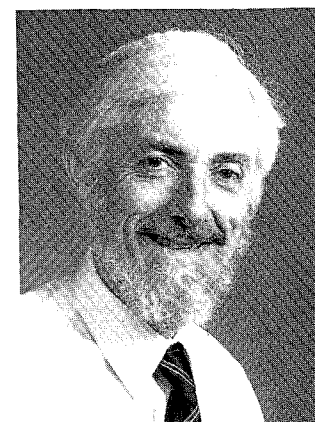
Daniel R. Glen



Steve L. Golledge



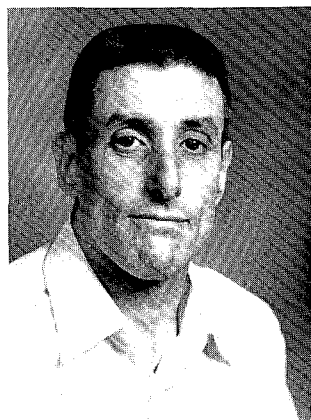
Dr. Gerald F. Hoff



Dr. Stanley D. James



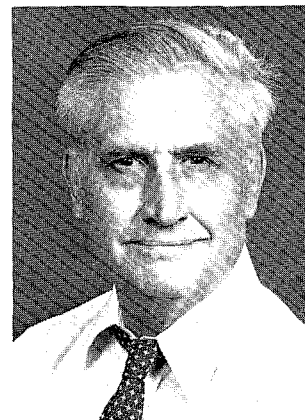
Dr. Donald E. Jones



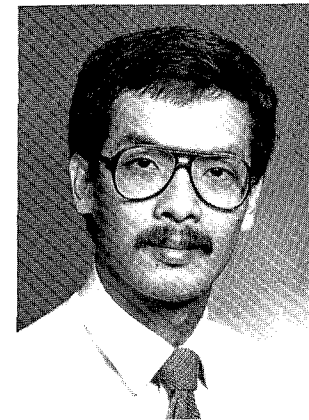
Dr. William P. Kilroy



Leonard A. Kowalchik



Benjamin F. Larrick



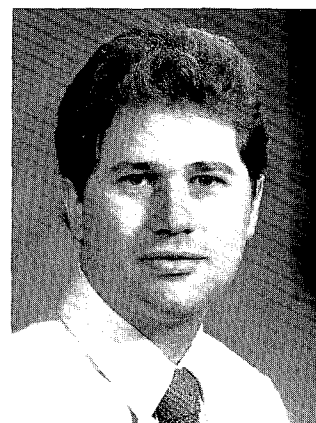
Dr. Anh H. Le



Dr. Jack F. McIntyre



Maurice F. Murphy



Timothy Murphy



Kathleen M. O'Neill



Laury F. Reid



Dr. Patricia H. Smith



Morton Stimler



Donald L. Warburton